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(54) Antimicrobial dish washing liquid.

(57) Herein is disclosed a nonionic aqueous dishwashing liquid that has good foaming capability and antibacterial action. The liquid contains:

a) 0.5 to 15, preferably 2, weight percent of a quaternary disinfecting compound;
b) 0.5 to 20, preferably 13-14, weight percent of a C_{12}-C_{13} alcohol ethoxylate nonionic surfactant;
c) 0.0 to 20, preferably 3-5, weight percent of a C_{13}- C_{15} alcohol ethoxylate nonionic surfactant;
d) 0.5 to 20.0, preferably 2, weight percent of a nonionic surfactant selected from the group consisting of cocomonoethanolamide or cocodiethanolamide or combinations thereof;
e) 0.5 to 12, preferably 4-5, weight percent cocoamidopropyl betaine nonionic surfactant;
f) 0 to 2.0, preferably 1, weight percent of the sodium salts of EDTA.

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This invention relates to formulations for manually washing dishes.

Light-duty liquid detergent formulations for kitchen surfaces are well known. Kitchen surfaces include counter tops, stove tops, dishes and any other hard surface commonly found in kitchen environments. The term "dishes" includes any utensils involved in food preparation or consumption. Kitchen surfaces, particularly dishes, must be washed free of food residues, grease, proteins, starches, gums, dyes, oils and burnt organic residues.

Most of the consumer accepted formulations in use include anionic synthetic surfactants with or without a nonionic surfactant. Many of such formulations contain a sulphonate-type anionic surfactant, for example, an alkylbenzene sulphonate or an alkane sulfonate, in conjunction with a sulphate or alkyl ether sulphate, or a nonionic surfactant, for example, an alcohol ethoxylate, an alkyl phenol ethoxylate, a mono- or diethanolamide or an amine oxide. The sulphonate material generally predominates.

It is the anionic surfactant that provides the typical high foaming (suds) characteristics generally associated with dish washing formulations. Foam (suds) is the cleaning efficacy signal relied on by consumers. Nonionic surfactants generally do not provide good foaming characteristics.

It is known from US-A-2,746,928 that it is not possible to mix anionic surface-active agents with quaternary ammonium germicides. The cationic quaternary ammonium germicide reacts with the anionic surface-active agent resulting in a reduction in germicidal and detergent activity.

Thus anionic surfactants are incompatible with cationic quaternary antimicrobial surfactants and non-ionic surfactants do not normally provide significant foaming capability to liquid formulations. Therefore current dish washing formulations can only mechanically eliminate bacteria from kitchen hard surfaces. They are not effective in killing or controlling the spread of germs throughout the kitchen environment. Thus dish washing liquids combining good foaming and antimicrobial activities are not available to the consumer.

The present invention provides an aqueous disinfecting liquid formulation for cleaning hard surfaces, particularly dishes, in a kitchen environment; wherein said formulation is free of anionic surfactants and consisting essentially of:

a) 0.5 to 15 weight percent of a quaternary disinfecting compound;

b) 0.5 to 20, preferably 13 to 14, weight percent of a C_{12}-C_{13} alcohol ethoxylate nonionic surfactant;

c) 0.0 to 20, preferably 3 .0 to 5, weight percent of a C_{13}- C_{15} alcohol ethoxylate nonionic surfactant;

d) 0.5 to 20.0, preferably 2, weight percent of a nonionic surfactant selected from the group consisting of cocomonoethanolamide, cocodiethanolamide and combinations thereof;

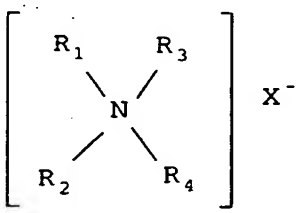
e) 0.5 to 12, preferably 3.0 to 9.0, weight percent cocoamidopropyl betaine nonionic surfactant;

f) 0 to 2.0, preferably 1.0, weight percent of the sodium salts of EDTA.

This formulation of this invention will control the presence and spread of bacteria on hard surfaces in the kitchen environment, especially dishes. This invention contains a microbiologically active quaternary ingredient homogeneously incorporated into a nonionic aqueous surfactant system. Unexpectedly the formulation has good flash foaming and residual foaming capability although no anionic surfactants are included. Moreover, the formulation has excellent viscosity and color stability.

Optional ingredients can include fragrances, dyes and stabilizers.

The purpose of the quaternary ammmonium disinfectants is to kill on contact gram positive and gram negative organisms the organisms encountered in kitchen environments. Useful disinfectants include BTC 8358 which is N- Alkyl (50% C_{14}, 40% C_{12}, and 10% C_{16}) dimethyl benzyl ammonium chloride. Other quaternary ammonium salt may be any of the well-known class of quaternary ammonium germicides characterized by the formula:



wherein at least one of the radicals R_1, R_2, R_3 and R_4 is a hydrophobic, aliphatic, aryl aliphatic, or aliphatic aryl radical of from 6 to 26 carbon atoms and the entire cation portion of the molecule has a molecular weight of at least 165. The hydrophobic radicals may be long-chain alkyl, long-chain alkoxy aryl, long-chain

alkyl aryl, halogen-substituted long-chain alkyl aryl, long-chain alkyl phenoxy alkyl, aryl alkyl, and so forth, in nature. The remaining radicals on the nitrogen atom other than the hydrophobic radicals are substituents of hydrocarbon structure usually containing a total of no more than 12 carbon atoms. The radical X in the above formula is any salt-forming anionic radical.

Suitable quaternary ammonium salts within the above description include the alkyl ammonium halides such as cetyl trimethyl ammonium bromide, alkyl aryl ammonium halides such as octadecyl dimethyl benzyl ammonium bromide, N-alkyl pyridinium halides such as N-cetyl pyridinium bromide, and the like. Other suitable types of quaternary ammonium salts include those in which the molecule contains either, amide or ester linkages such as octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, N-(laurylcocoaminoformylmethyl) - pyridinium chloride, and so forth. Other very effective types of quaternary ammonium germicides are those in which the hydrophobic radical is characterized by a substituted aromatic nucleus as in the case of lauryloxyphenyltrimethyl ammonium chloride, cetylaminophenyltrimethyl ammonium methosulfate, dodecylphenyltrimethyl ammonium methosulfate, dodecylbenzyltrimethyl ammonium chloride, chlorinated dodecylbenzyltrimethyl ammonium chloride, and the like.

Preferred quaternary ammonium germicides of the above general types are the long-chain alkyl dimethylbenzyl quaternary ammonium salts, the alkyl phenoxy alkoxy alkyl dimethyl benzyl quaternary ammonium salts, the N-(acylcocoaminoformylmethyl)pyridinium halides, the long-chain alkyl trimethyl ammonium halides, the long-chain alkyl benzyl dimethyl benzyl ammonium halides, and the long-chain alkyl benzyl diethyl ethanol ammonium halides in which the alkyl radical contains from 8-18 carbon atoms.

The mechanism of this nonionic system for cleaning standard food and kitchen soils is through emulsification of the soils. Current anionic light duty liquids solubilize most food soils. When soil is emulsified within a system, it will affect the type, density and amount of foam that can be generated. In general, emulsified fatty soils will reduce the amount of foam that can be generated as further cleaning takes place. Since anionic systems solubilize soils, the effect on the foam is not as great as with nonionic systems. Therefore, foam generated from anionic systems is of greater volume and more stable throughout the cleaning process.

In general, anionic surfactant systems such as those found in the current light duty liquids are classified as high foamers. Conversely, nonionic surfactant systems are classified as low foamers.

The challenge was to achieve disinfection activity while producing consumer acceptable foam using a nonionic and cationic surfactant combination. By careful selection and great experimentation, we have identified a surfactant mixture, expressed in Example 1, Table 1, that produce consumer acceptable foam comparable to commercial dish washing liquids using anionic detergents. The useful nonionic surfactants have various chain lengths and degrees of ethoxylation that allow the dish washing liquid to be effective on a wide range of food soils while providing good flash foam volume as well as moderate foam stability. This system provides the consumer with effective cleaning on, but not limited to, greasy food soils, fatty food soils, and oily food soils while maintaining disinfection.

Example 1-3

The unexpected foaming properties of the formulations of the invention are illustrated in these examples. The foaming properties are due to the carefully balanced mix of nonionic surfactants. The formulations of examples 1-3 are presented in Table 1.

Table I

INGREDIENTS	Content in the Weight Percent		
	Example 1	Example 2	Example 3
WATER, D.I	62.95%	64.05%	61.95%
DISODIUM EDTA	1.00%	1.00%	1.00%
NEODOL 25-12	------	4.00%	3.00%
NEODOL 23-6.5	14.00%	13.00%	13.00%
MACKAM DZ (30%)	16.70%	13.60%	16.70%
MACKAMIDE C	3.00%	------	------
MONAMID CMA	------	2.00%	2.00%
BTC 8358 (80%)	2.00%	2.00%	2.00%
FRAGRANCE	0.35%	0.35%	0.35%
24 HR. *VISCOSITY	610 CPS	712 CPS	766 CPS
6 WEEKS ROOM TEMP. *VISCOSITY	618 CPS	728 CPS	734 CPS

*Brookfield Model LVT, spindle 3 at 60 rpm

The formulations were prepared by adding the ingredients to ambient temperature water in the order described and mixed until dissolved. Alternatively, if Monamid CMA is used (examples 2 & 3 above), the mixture is warmed to about 100 °F before the addition of Monamid CMA to aid dissolution. Other known methods may be used know to those skilled in the art. The batch can then be cooled down to add any volatile components.

The chemical name and function of each ingredient in Table I is presented below in Table II.

Table II

TRADENAME	CHEMICAL NAME	FUNCTION
D.I. WATER	DEIONIZED WATER	DILUENT
MACKAMIDE C	COCOAMIDE DEA (cocodiethanol amide)	NONIONIC SURFACTANT
MONAMID CMA	COCOAMIDE MEA (cocomonoethanol amide)	NONIONIC SURFACTANT
NEOPOL 25-12	C_{13}-C_{15} ALCOHOL ETHOXYLATE	NONIONIC SURFACTANT
NEOPOL 23-6.5	C_{12}-C_{13} ALCOHOL ETHOXYLATE	NONIONIC SURFACTANT
MACKAM DZ (30-35%)	COCOAMIDOPROPYL BETAINE	NONIONIC SURFACTANT
DISODIUM EDTA	DISODIUM EDTA	CHELATOR
BTC 8358 (80%)	N-ALKYL DIMETHYL BENZYL AMMONIUM CHLORIDE	GERMICIDE

The good foaming capability is established by measuring foam height according to the Standard Test method for Foaming Properties of Surface-Active Agents, ASTM D1173-53 (Reapproved 1986). The method was modified by using a 500 mL cylinder as the foam receiver. Foam heights in the foam receiver were taken initially after the dropping of the solution and at various time intervals thereafter. Foam height was determined in both unloaded and loaded systems. A loaded system refers to water in which oil has been added to simulate oils encountered during dish washing. An unloaded system refers to water to which no oil has been added.

A second method for measuring foam heights was also utilized. This method, designed by the Shell Development Co., is entitled *Soil Titration Test for Determination of Foam Performance of Dish washing Detergents.* It was published January 1987 as SC:967-87. The method is a procedure to evaluate the foam performance of detergent formulations in the presence of dish washing soils. Foam heights are measured as a percent of a standard formulation.

Table III

FOAM HEIGHT STABILITY IN USE

Method Evaluation	Example 1 Minutes				Example 2 Minutes				Example 3 Minutes			
	0	5	10	15	0	5	10	15	0	5	10	15
Modified ASTM D1173-53 Foam Height (1:256.CM)												
Unloaded (cm)	15	14.5	14.5	14	15	14.5	14	14	16	15.5	15	13
Loaded (cm)	15	14.5	14	13.5	15	15	14	13.5	15.5	15	14.5	14
Soil Titration Test Foam Performance Rating, %	51				49				58			

The formulations of this invention were compared to commercial anionic based dish washing liquids using the modified ASTM D1173-53 method. In an unloaded soil system, foam heights ranged from 16 - 19 cm. In a loaded soil system, foam heights ranged from 13.5 - 15.5 cm. Our invention of a non-ionic compared quite favorably.

Examples 4-6

The formulation of example 3 was tested using various levels of active BTC 8358 for antimicrobial activity against Staphyloccus aureus (ATTC 6538) and Kleb pneumoniae (ATTC 4352) by a quantitative suspension test. The test was carried out at dilution of one part formulation to 256 parts of deionized water at room temperature for a 30 second contact time. The test protocol was as follows.

1. Sample Inoculation

A. Inoculate 1.0 ml of the test culture into each sample tube. Repeat for organism.
B. Subculture 1.0 ml of the sample after 1-minute and 1.0 ml after 5 minute contact time.
C. Subculture the sample into 9.0 ml of DIFCO AOAC Letheen Broth. This the 10^{-1} sample dilution.

2. Sample Dilutions and Plating

A. Plate the 10^{-1}, 10^{-3}, and 10^{-5} dilutions for each sample/organism/contact time combination.
   1. From the 10^{-1} dilution:
      a. Plate 1.0 ml = 10^{-1} plate.
      b. Pipet and transfer 0.1 ml into 9.9 ml of Letheen Broth = 10^{-3} sample dilution.
   2. From the 10^{-3} sample dilution:
      a. Plate 1.0 ml = 10^{-3} plate.
      b. Pipet and transfer 0.1 ml into 9.9 ml of Letheen Broth = 10^{-5} sample dilution.
B. Pour each plate with Tryptic Soy Agar containing polysorbate 80 and lecithin (either DIFCO or BBL).
C. Incubate the plates for 48hr at 35C.

3. Control Counts: Dilutions and Plating

A. Inoculate 1.0 ml of culture into 9.0 ml Letheen Broth.
B. Subculture 1.0 ml of that Letheen tube into 9.0 ml Letheen Broth at 1 minute and 5 minutes exposure. These are the 10^{-1} dilution tubes for the 1-minute and 5-minute contact time controls.
C. Plate the 10^{-4} and 10^{-5} dilutions for each contact time.
   1. Pipet 0.1 ml of the 10^{-1} dilution into 9.9 ml Letheen Broth = 10^{-3}.
   2. Plate 0.1 ml of the 10^{-3} dilution = 10^{-4} plate.

3. Pipet 0.1 ml of the 10^{-3} dilution into 9.9 ml of Letheen Broth = 10^{-5} dilution.
4. Plate 1.0 ml of the 10^{-5} dilution = 10^{-5} plate.

D. Pour the plates with Tryptic Soy Agar containing polysorbate 80 and lecithin.
E. Incubate at 35 • C for 48hr.

4. Log Reduction Calculations

A. Determine the number of bacteria survivors at each contact time for both the controls and test samples.
1. Count the number of colonies on the petri dish. The plate is acceptable for counting with a colony count between 25 and 250.
2. Multiply the number of colonies by the plate dilution factor = the number of surviving bacteria.

B. Determine the Log Reduction in bacteria for each sample/organism/contact time combination. Log_{10} Control Count - Log_{10} Survivor Count = # Logs of bacteria reduced by the sample.
The results obtained are presented in Table IV.

TABLE IV

PERCENT OF BACTERIAL REDUCTION AT 30 SECOND CONTACT TIME				
MICROBIOLOGY TEST NUMBER	% BTC 8358 IN FORMULA (ACTIVE)	DILUTION	Percent Reduction of S. Aureus	Percent Reduction of Kleb. Pneumoniae
(Control)	0.00	1:256	83.1818	47.6623
1	0.50	1:256	85.4545	77.9220
2	1.00	1:256	87.2727	76.6233
3	1.50	1:256	95.0909	88.9610
4	2.00	1:256	94.1818	94.1558
5	2.50	1:256	97.6818	97.3766
7	3.00	1:256	99.4363	98.9090
8	3.50	1:256	99.8772	99.7441
9	4.00	1:256	99.992	99.8481

Claims

1. An aqueous disinfecting liquid formulation for cleaning hard surfaces in a kitchen environment; wherein the formulation is free of anionic surfactants and consisting essentially of:
a) 0.5 to 15 weight percent of a quaternary disinfecting compound;
b) 0.5 to 20 weight percent of a C_{12}-C_{13} alcohol ethoxylate nonionic surfactant;
c) 0.0 to 20 weight percent of a C_{13}- C_{15} alcohol ethoxylate nonionic surfactant;
d) 0.5 to 20.0 weight percent of a nonionic surfactant selected from the group consisting of cocomonoethanolamide, cocodiethanolamide and combinations thereof;
e) 0.5 to 12 weight percent cocoamidopropyl betaine nonionic surfactant;
f) 0 to 2.0 weight percent of the sodium salts of EDTA.

2. The formulation of claim 1 consisting essentially of
a) 2 weight percent of a quaternary disinfecting compound;
b) 13 to 14 weight percent of a C_{12}-C_{13} alcohol ethoxylate nonionic surfactant;
c) 3.0 to 5 weight percent of a C_{13}- C_{15} alcohol ethoxylate nonionic surfactant;
d) 2 weight percent of a nonionic surfactant selected from the group consisting of cocomonoethanolamide, cocodiethanolamide and combinations thereof;
e) 3.0 to 9.0 weight percent cocoamidopropyl betaine nonionic surfactant;
f) 1.0 weight percent of the sodium salts of EDTA.

3. The formulation of claim 1 or 2 wherein the quaternary disinfecting compound is alkyl (50% C^{14}, 40% C_{12} and 10% C_{16}) dimethyl benzyl ammonium chloride.

4. The formulation of any one of the preceding claims having a viscosity of 250 to 1000 CPS.

5. The formulation of any one of the preceding claims having a viscosity of 250 to 800 CPS.

6. A method of manually washing hard surfaces in a kitchen environment, comprising the steps of:
   a) providing a disinfecting liquid according to any one of the preceding claims;
   b) diluting the liquid with water; and
   c) contacting the surfaces with the diluted formulation.

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(54) Antimicrobial dish washing liquid.

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a) 0.5 to 15, preferably 2, weight percent of a quaternary disinfecting compound;

b) 0.5 to 20, preferably 13-14, weight percent of a C_{12}-C_{13} alcohol ethoxylate nonionic surfactant;

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e) 0.5 to 12, preferably 4-5, weight percent cocoamidopropyl betaine nonionic surfactant;

f) 0 to 2.0, preferably 1, weight percent of the sodium salts of EDTA.

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EUROPEAN SEARCH REPORT

Application Number
EP 94 20 3079

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	GB-A-2 075 043 (J.J.FLANAGAN) * the whole document * ---	1-3	C11D1/835 C11D3/48 C11D3/00 C11D1/94 C11D3/33
A	EP-A-0 004 121 (PROCTER & GAMBLE CO.) * page 35; example xi * * claims * ---	1-3	
A	US-A-3 983 079 (G.L.SPADINI ET AL.) * the whole document * ---	1-3	
A	EP-A-0 152 194 (PROCTER & GAMBLE CO.) * claims * ---	1	
A	DATABASE WPI Week 9035, Derwent Publications Ltd., London, GB; AN 90-264444 & JP-A-2 184 609 (SANYO CHEM IND LTD) 19 July 1990 * abstract * ---	1	
A	EP-A-0 275 478 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN) * claims * -----	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	10 August 1995	Pelli Wablat, B

CATEGORY OF CITED DOCUMENTS

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